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DEVELOPMENT OF SILVER-ZINC CELLS OF IMPROVED CYCLE LIFE AND ENERGY DENSITY

BY ROBERTO SERENYI (YARDNEY TECHNICAL PRODUCTS, INC.)

EDITED AND REVIEWED BY DR. STANLEY D. JAMES (NSWCDD)

FOR NAVAL SURFACE WARFARE CENTER, DAHLGREN DIVISION
WEAPONS RESEARCH AND TECHNOLOGY DEPARTMENT

3 MARCH 1994

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Silver Spring, Maryland 20903-5640

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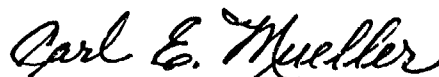
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FOREWORD

This report describes a Small Business Innovative Research (SBIR) Phase I program sponsored by the Office of Naval Research. It was conducted under Contract Number N60921-91-C-0205, which was awarded to Yardney Technical Products, Inc., by the Naval Surface Warfare Center Dahlgren Division's (NSWCDD's) White Oak Detachment in Silver Spring, Maryland. The work was performed during the period from 16 August 1991 through 15 January 1992 under the direction of the principal investigator and author of this document, Mr. Roberto Serenyi. NSWCDD's Dr. Stanley James of the Electrochemistry Branch (Code R33) served as the Contracting Officer's Technical Representative and also edited this report.

The author wishes to thank Mr. Franz Goebel for his technical guidance, Mr. Jerry Kuklinski for developing methods of negative electrode manufacture, and Mr. Fred Thompson for directing the electrical tests on the cells.

Approved by:



CARL E. MUELLER, Head
Materials Division

ABSTRACT

Substantial increases in the cost effectiveness and range of naval underwater vehicles are possible by virtue of advances made, in this program, in silver-zinc, vehicle propulsion batteries. The higher battery energy density translates to a 70 percent longer vehicle run time. Significant dollar savings are possible because increased battery cycle life will permit 70 percent more vehicle missions before the very expensive batteries must be discarded.

This SBIR program was designed to improve the cycle life and energy density of silver-zinc cells, especially those used in naval propulsion systems, by advancing the state-of-the-art of the negative electrodes and the separators, which are responsible for most of the shortcomings of that electrochemical couple.

To achieve those objectives, Yardney Technical Products, Inc. (YTP), has relied mostly on a new class of materials, known as Electro-Permeable Membranes (EPMs), covered by U.S. Patent No. 4,797,190, issued to Mr. Robert L. Peck. These materials are used as additives and/or as coatings for the negative electrodes and also as coatings for conventional separator materials. Moreover, YTP has tested bismuth oxide as an additive to the negative electrodes and P2291-40/20, a radiation-grafted polyethylene film, as a separator used in conjunction with C-19, YTP's brand of silver-treated cellophane.

The use of EPMs as negative-electrode additives and also as coatings for Celgard 2500 microporous polypropylene (three turns) provided greatly improved cells with 68 percent longer cycle lives (160 vs. 95), 38 percent better utilization of active materials, and 70 percent better capacities when compared with standard cells after 90 cycles.

However, cells with EPMs used as a coating for the negative electrodes failed rapidly because of an error in formulation.

Cells with 10 percent bismuth oxide in the negative electrodes exhibited substantially lower capacity than the standard cells and were removed from the test.

Cells with radiation-grafted polyethylene separators provided fewer cycles than the standard cells (81 vs. 95), with 5 percent higher capacity and 6 percent lower utilization of active materials by cycle 60. In summary, the slightly increased capacity of these cells, realized due to the additional space available for active materials, does not compensate for their generally unimpressive performance.

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CHAPTER 1

INTRODUCTION

Although the silver-zinc system was known since the famous experiments of Alessandro Volta in 1796, all attempts at building rechargeable cells of this electrochemistry failed until the 1940's when the French professor Henry Andre came upon the idea of using cellophane as a separator material for the cell. Additional development work by Andre and others resulted in a truly rechargeable, commercially viable, silver-zinc cell that has been in use ever since for a long list of military, space, and commercial applications such as: propulsion for small submersibles, undersea rescue vehicles, torpedoes, and targets; communications; short bursts of very high power (Strategic Defense Initiative); missiles (for telemetry, control, rocket-stage separation, self-destruct capability); lunar exploration, astronaut's extravehicular activities, and orbital maneuvering vehicles; television cameras and recorders; surgical instruments; pipeline inspection crawlers; and many more.

BACKGROUND INFORMATION

Present state-of-the-art silver-zinc cells offer the highest energy density among the commercially viable rechargeable batteries (up to 250 Wh/kg), the highest power density (up to 800 W/kg for continuous discharges and 3000 W/kg for short-duration pulses), a relatively low self-discharge rate (3 to 8 percent per month at 25 °C, depending on cell design) and a flat voltage during most of the discharge. However, they suffer from two serious drawbacks:

- A relatively short wet life (maximum of two to three years)
- Relatively rapid capacity degradation, which limits the number of useful cycles to 50-150 (or the equivalent number of shallow cycles)

These shortcomings are mostly due to the deficiencies of two of the cell components: the zinc electrode and the separators.

The Zinc Electrode

This component of the silver-zinc system is responsible for the above cycling limitations. The major reasons are shape change and the formation of zinc dendrites.

Shape Change. Shape change is a phenomenon whereby zinc oxide, formed during the discharge, is partially dissolved in the electrolyte and redeposited during

the charge in a location different from where it originated. The result is a gradual depletion of the active material at the top and edges of the electrode, which eventually lose all electrochemical activity, while the bottom and center absorb the excess and increase their density, which also decreases activity. As a consequence of shape change, silver-zinc cells lose 50 percent of their initial capacity in about 50 to 150 cycles, depending on their designs and modes of operation. Within that range, capacity losses occur faster when cells are operated at high charge and/or discharge current densities.

Past attempts at reducing shape change have been only marginally successful. These include the following:

- Use of excess zinc over the amount required for stoichiometric equilibrium with the positive active material. This is currently a standard practice; the excess ranges from 20 to 70 percent, depending on cycle-life requirements.
- Inclusion of additives and binders. Some of these, such as Teflon, neoprene, and potassium titanate fibers, are mildly effective against shape change.
- Other more exotic methods (e.g.: contoured negatives, forced electrolyte circulation) are of theoretical interest but impractical from a cost/benefit viewpoint.

Zinc Dendrites. Zinc dendrites (needles) are a crystalline form of the metal that is produced during overcharge. These dendrites may puncture the separators, causing irreversible cell failure by internal short circuits. The following are several methods of preventing formation of zinc dendrites:

- Careful charge control, including termination of the charge at lower than normal battery voltage or, preferably, individual cell voltage monitoring. This method is effective at the price of a small sacrifice of output capacity but requires the constant attention of personnel or costly automatic equipment.
- Use of excess negative material so that the negative electrodes are not overcharged. However, as cycling progresses, this excess is depleted until the cell becomes zinc-limited on charge due to the shape change of the zinc or to accidental overcharge. From this time on, the risk of dendrite formation is the highest.
- Nonconventional charge methods (e.g., pulse charging).

The Separators

Regenerated cellulose in various forms (plain or treated cellophane, fibrous sausage casing) has been used as the main separator for silver-zinc cells since the early days of the development of the system. Indeed it is nearly ideal in many respects, but it suffers from one serious weakness--limited resistance to oxidation by silver oxides, by oxygen, and by the electrolyte. As a result, the life of silver-zinc cells built with regenerated cellulose is practically limited to about two to three years, although some tested under laboratory conditions have lasted over four years.

Another type of separator, developed during the late 1960s and 1970s, consists of a polyethylene film that must be grafted and/or cross-linked by chemical treatment or irradiation to be converted into a useful semipermeable membrane.

Finally, another category of separators was introduced in the late 1970s--the microporous polypropylenes. These materials offer some distinctive advantages over the cellulose. They have lower electrolytic resistance and a high resistance to oxidative degradation--and they are very thin, allowing for significant gains in energy density by creating more space for active materials.

CHAPTER 2

TECHNICAL OBJECTIVES

The main technical objective of the program is the advancement of the state-of-the-art of the silver oxide-zinc system through improvements to the negative electrode and the separators.

IMPROVEMENTS TO THE NEGATIVE ELECTRODE

As may be surmised from Yardney Technical Product's (YTP's) previous discussion, this is not an easy task. All earlier attempts to achieve anything more than modest improvements were unsuccessful or, in the case of recently published work, remain unproven.

However, YTP believes that substantial improvements could be achieved that would extend the life of the silver-zinc system by a factor of two or better. For that purpose, YTP relied for most of the work (not only for the negative electrode but also for the separators) on a new class of materials known as Electro-Permeable Membranes (EPMs), which were invented by Mr. Robert L. Peck of T&G Corporation, a small business concern located in Lebanon, Connecticut.

T&G Corporation has been working in the area of ionic semiconductors for ten years and has been issued a fundamental patent on the subject (U.S. No. 4,797,190, January 1989) that not only describes the formulations of various semiconductors but also some unique electrochemical applications, including rechargeable zinc electrodes and separators. EPMs differ from existing manufactured membranes in that they are not porous and do not exhibit the normal diffusion, dialysis, osmosis, or Donnan effects associated with porous membranes. They are made from readily available polymers and may be processed with conventional production equipment into extruded or cast films.

EPMs are the analog of biological membranes which can keep two different solutions or electrolytes separated indefinitely yet can freely transfer selected ions. These membranes are not passive and do not rely upon external driving forces such as pressure or concentration differences for ion transfer. Rather, they utilize an inner dynamic transfer mechanism driven by heat obtained from the surrounding environment. EPM materials have been described as ionic semiconductors and are the ionic analog of electronic semiconductors, which are also driven by heat.

EPM material consists of a two-polymer blend. One of the polymers is a long chain hydrogel such as used to thicken solutions or to form gels, while the other polymer is a supporting material and can be one of the common plastics such as

polypropylene, polyvinyl chloride (PVC), or polyvinylidene fluoride (PVDF). There is a broad range of hydrogels and plastics that can be used.

For use in silver-zinc negative electrodes, various EPM formulations were coated on zinc-oxide particles to provide encapsulated domains expected to remain stable during charge and discharge, thereby maintaining a stable electrode morphology.

In addition, YTP manufactured and tested negative electrodes containing bismuth oxide because of the favorable results reported in the literature with this additive.

IMPROVEMENTS TO THE SEPARATORS

The useful life of silver-zinc cells is normally limited by the cycle life of the zinc negative electrode. Thus there has been little incentive to search for often costly, long-lasting separators, except for those relatively rare applications requiring long activated lifetimes but only a few cycles. However, as soon as substantial advances in zinc electrode technology are accomplished, the need for improved separators will be felt immediately. Again, YTP relied heavily on the EPMs for this purpose by coating them onto existing separator materials. The films that were applied were the following:

- Cellophane, still predominant in rechargeable silver-zinc cells; only one side of the film was coated.
- Celgard 2500, a 1-mil microporous polypropylene (with 45 percent porosity), which in its natural form is hydrophobic and therefore unsuitable as a separator for aqueous electrolyte batteries. The high-water-chain-content EPMs impart good ionic conductivity to these separators while their negligible diffusion rate restricts electrolyte mobility to a minimum, which should minimize the shape change of the zinc electrode. Both sides of the film were coated.

In addition, YTP tested a radiation-grafted polyethylene ion exchange membrane, code named F2291-40/20, that had undergone special processing to increase resistance to silver migration (developed by Pall RAI, Inc., Hauppauge, New York).

CHAPTER 3

EXPERIMENTAL

The work on this research program was divided into seven tasks, which are detailed in the following subsections.

TASK 1: DEVELOPMENT AND PREPARATION OF EPM FORMULATIONS FOR THE NEGATIVE ELECTRODE AND THE SEPARATORS

This task was performed by Mr. Robert Peck of T&G Corporation as part of his continuous effort to improve EPMs for electrochemical uses. As a result, in the time elapsed since YTP's proposal, new formulations of EPMs and a simplified method of applying them to the negative electrodes were developed. Preliminary tests, performed by Mr. Peck at the electrode level and by YTP at the cell level, indicated that the new formulations are indeed an improvement over those cited in the proposal both in terms of performance and ease of manufacture. For these reasons YTP decided to use the latest formulations, which are listed below after their intended purposes:

- For composite electrodes* with water-based EPMs: No. 2010
- For composite electrodes* with solvent-based EPMs: No. 2029
- For coated negatives: EPM No. 2029
- For coating Celgard 2500: EPM No. 2525
- For coating cellophane:** EPM No. 2526

* Composite electrodes were also coated with EPM No. 2029.

** At the recommendation of Mr. Peck, YTP decided to coat plain cellophane rather than C-19 (YTP's proprietary, silver-treated cellophane) as originally planned because of possible adverse effects of the reaction of the silver with the EPMs.

TASK 2: DEVELOPMENT OF A PROCEDURE FOR THE MANUFACTURE OF SMALL QUANTITIES OF NEGATIVE ELECTRODES WITH EPMs AND Bi₂O₃. EXTENSION TO PILOT PLANT QUANTITIES

Step 1

Composite negative electrodes with solvent-based EPM were made by thoroughly mixing the ZnO and the EPM, grinding it and sifting it through a 20-mesh sieve to separate any clumps, spreading half of a predetermined amount of the mix into the cavity of a mold, placing a precut piece of silver exmet on top, spreading the remaining half over the grid, and pressing it to the desired thickness. After removal from the mold, the plates were oven dried overnight at 60 °C, which was sufficient to evaporate all of the solvent as evidenced by the absence of further weight loss when drying was continued. The plates so obtained were mechanically strong and of uniform weight and thickness.

The materials used per plate were the following:

- Zinc-oxide powder, USP grade, particle size 0.4 - 0.6 microns, in the proportion of 91.5 percent by dry weight.
- EPM No. 2029 suspension (17 percent by weight solids) in the proportion required to obtain 8.5 percent by weight of solids after evaporation of the solvent.
- Expanded metal, type 5Ag 7-3/0, 1.47 inch x 2.22 inches, with 2-0.016-inch diameter silver wires welded on.

Step 2

Composite negative electrodes with water-based EPM (No. 2010) were made by a process similar to that described above, except that the ZnO and the EPMs were preheated to about 50 °C to obtain a homogeneous mixture. These plates were also mechanically strong.

The materials used per plate were:

- Zinc oxide powder, as in Step 1 above, in the proportion of 94.0 percent by dry weight.
- EPM No. 2010 suspension (17 percent by weight solids) in the proportion required to end up with 6.0 percent by weight of solids after evaporation of the water.
- Expanded metal, as in Step 1 above.

Step 3

The manufacture of negative electrodes with 90 percent ZnO and 10 percent Bi₂O₃ was accomplished by the same method as used for YTP's standard zinc-oxide plates. The method consists of mixing the zinc-oxide and bismuth oxide with a

chemical binder, a fibrous mechanical binder, and enough water to form a paste of the desired consistency, which is spread onto the conveyor belt of a pasting machine, doctored to the desired area density to form a continuous strip, dried to evaporate all the water, and cut into large sheets. These sheets are then cut to plate size and pressed (one on each side of the collector--a perforated silver foil with the leads prewelded) to the required thickness to form a finished electrode.

The ease of manufacture of these electrodes is an advantage; the process is inexpensive and ready for pilot plant and mass production quantities.

Step 4

The extension of the manufacturing techniques for negative electrodes containing EPMs to pilot plant quantities can easily be achieved by the following:

- Use of a low-speed blender for mixing the powders,
- Use of multiple cavity molds, and
- Use of a hydraulic press with kiss blocks and predetermined tonnage.

YTP has also attempted to extend some techniques to large-scale production with mixed results.

YTP produced a fair quantity of electrodes with water-based EPMs by pasting in a manner similar to that described for its standard electrodes. After generating a large quantity of rejects, YTP was able to adjust the parameters so as to produce acceptable plates; however, they were not quite as sturdy as desired and had less than the optimum concentration of EPMs. Additional work in this area is needed, but it is beyond the scope of Phase I of this program. It should be noted that none of the electrodes produced in this way were used to build cells for this program.

TASK 3: MATERIALS AND EQUIPMENT

The following materials and equipment were obtained specifically for this program:

- EPMs as listed in Chapter 3, Task 1
- 12-Ah cell cases, molded in styrene acrylonitrile (SAN), which is transparent (instead of acrylonitrile butadiene styrene [ABS], which is opaque)
- Celgard 2500 (Hoechst Celanese, Separation Products Division)
- Bismuth oxide, 99.9 percent (Aldrich Chemical Co., catalog No. 22,389-1)
- P2291-40/20 separator (Pall RAI, Inc.)
- Stainless steel molds, 1.50 inch by 2.25 inches, for processing negative electrodes (manufactured by YTP's machine shop)

The following is a partial list of on-hand materials and equipment used for this program:

- Silver powder, high capacity (HC) grade (YTP)
- Silver Exmet 5Ag 7-3/0 (Exmet Corp., Bridgeport, CT)
- .016-inch-diameter silver wire
- Zinc oxide powder (refer to Chapter 3, Task 2)
- Mercuric oxide, yellow, American Chemical Society (ACS) grade
- 12-Ah cell covers and hardware
- Cellophane (Flexel, Inc., style 195PUTSD2)
- C-19 (YTP)
- Woven and nonwoven nylon (Pellon)
- Computerized automatic cycler, designed around a Fluke Helios data acquisition unit, controlled by a Hewlett-Packard Vectra QA/165 computer. The cycler is capable of running a maximum of 32 cells divided into four independent programmable test stations. Current for each station is controlled by programming a Transistor Devices Model No. DML50-20-100 load.

TASK 4: COATING OF CELGARD 2500 AND CELLOPHANE WITH EPMs

These separators were cut into large sheets, sent to T&G Corporation for coating with EPMs (No. 2525 for Celgard and No. 2526 for cellophane), and returned to YTP for trimming to size and use in cell assembly.

TASK 5: SCREENING TESTS ON SEPARATORS

Screening tests were performed on all nonconventional separators used in the program; results are shown in Table 1. Also included in the table (for reference) are typical values for C-19, YTP's proprietary silver-treated cellophane. It should be noted that the high resistance figures for EPM-coated separators probably arise from their slow response to the 40-Hz square wave pulse current used to measure them and may not be used to predict the load voltage of cells built with them (as would be the case with traditional separators).

TABLE 1. SCREENING TESTS ON SEPARATORS

Separator	C2500 ⁽¹⁾	Cello ⁽²⁾	RAI ⁽³⁾	C-18 ⁽⁴⁾
Thickness, dry (mils)	1.5	1.7	1.6	1.1
Thickness, wet (mils)	1.2	2.4	1.9	3.2
Resistance ($m\Omega \times in^2$) ⁽⁵⁾	230	66	26	13
Expansion (%) ⁽⁶⁾	0 x 0.5	0 x 2	13 x 8	0 x 8

Notes:

- [1] Celgard 2500, coated with EPM No. 2525
- [2] Cellophane, coated with EPM No. 2526
- [3] RAI style P-2291 40/20 (radiation-grafted polyethylene)
- [4] typical
- [5] in 42 percent KOH
- [6] in two perpendicular directions

TASK 6: CELL DESIGN AND MANUFACTURE

For the cell design part of this task, YTP followed, in general, the guidelines of the SBIR proposal but introduced several modifications to optimize the designs and take maximum advantage of the benefits that the new technology is expected to bring about, including the following:

- The latest EPM formulations were used (refer to Chapter 3, Task 1).
- An increased number of cells (36 vs. 28) was used.
- Two variations of standard cells (with and without HgO in the negatives) were used.
- All cells, including the standards, used a bag of nonwoven nylon (Pellon) around the negatives.
- All cell packs occupied the entire depth of the 12-Ah cell cavity without shims. As a result, the cells had variable amounts of active materials and were judged both in terms of overall capacity and capacity per gram of active silver.
- One variation with negatives containing Bi₂O₃ was added. (This was inadvertently left out of Table I of the SBIR proposal.)

Due to an experimental error, explained in detail in Chapter 5, the composition of the negative electrodes of the V2 cells was not as planned. To avoid confusion, all future references to variation V2 concern the cells as actually built, while the planned cells are designated as V2P. As a result of these modifications and the error, the cell design summary was changed as shown in Table 2 below:

TABLE 2. CELL DESIGN SUMMARY

Variation No.	Negative Electrode	Main Separator ^[5]
V1	Standard (1% HgO)	5T C-19
V1A	Standard (except no HgO)	5T C-19
V2	96.2% ZnO + 3.8% EPM No. 17K ^[1]	3T C2500, coated ^[3]
V2P	94.0% ZnO + 6.0% EPM No. 2010 ^[2]	3T C2500, coated ^[3]
V3	91.5% ZnO + 8.5% EPM No. 2029 ^[2]	3T C2500, coated ^[3]
V4	Coated with EPM No. 2029	5T C-19
V5	Coated with EPM No. 2029	3T cellophane, coated ^[4]
V6	Coated with EPM No. 2029	3T C2500, coated ^[3]
V7	Standard (1% HgO)	2T C-19 + 3T P-2291 40/20
V8	90% ZnO + 10% Bi ₂ O ₃	5T C-19

Notes:

- [1] refer to Chapter 5
- [2] also coated with EPM No. 2029
- [3] with EPM No. 2525
- [4] with EPM No. 2526
- [5] e.g., 5T C-19 means five layers (thicknesses) of C-19 separators were used

More complete details of the cell design are shown in Table 3. As may be seen, there are three different amounts of silver powder in the cells:

- 27.7 g for Variation Nos. 1, 1A, 4, and 8
- 30.3 g for Variation Nos. 5 and 7
- 34.0 g for Variation Nos. 2, 3, and 6

The amount of negative material has been kept constant at 85 percent of the active silver weight; however, the amount of active zinc varies from approximately 75 percent to approximately 85 percent because of differences in the percentage of additives. Note that the stoichiometric weight ratio of zinc to silver is 0.606 to 1.0 (60.6 percent).

TABLE 3. CELL DESIGN DETAILS

Denomination	V1/V1A[5]	V2	V2P	V3	V4	V5	V6	V7	V8
Positives, Number	4	→[9]	→	→	→	→	→	→	→
Collector	5 Ag 15-1	→	→	→	→	→	→	→	→
Powder (g)	27.7	34.0	34.0	34.0	27.7	30.3	34.0	30.3	27.7
Dimensions (in.)	1.50 x 2.25	→	→	→	→	→	→	→	→
Thickness (in.)	.027	.033	.033	.033	.027	.0295	.033	.0295	.027
Total Area (in. ²)	26.8	→	→	→	→	→	→	→	→
Negatives, Number	5(3f + 2h)[6]	→	→	→	→	→	→	→	→
Collector	.0015 Ag foil	5 Ag 7-3/0	→	→	.0015 Ag foil	→	→	→	→
Zinc (g)[1]	23.5	30.4	29.0	29.0	23.5	26.1	29.0	26.1	23.5
Additives	1% HgO[5]	3.8%-17K	6%-2010	8.5%-2029	—	—	—	1% HgO	10% Bi ₂ O ₃
Thickness (in.)[2]	.053/.0285	.064/.034	.064/.034	.064/.034	.053/.0285	.058/.031	.064/.034	.058/.031	.053/.0285
Construction	Rolled	Mold Press	Mold Press	→	Rolled	→	→	→	→
Coat	None	→	EPM 2029	→	→	→	→	none	→
K Ratio[3]	.85	.855	.80	.78	.85	.85	.85	.85	.765
Separator Wrap	5T C-19[7]	3T C2500	3T C2500	→	5T C-19	3T cello	3T C2500	2T C-19 + 3T P2291	5T C-19
Positive	1 P5-bag[8]	→	→	→	→	→	→	→	→
Negative	.548	.534	.534	.534	.548	.548	.534	.547	.548
Cell Pack, wet (in.)	.557-.560	→	→	→	→	→	→	→	→
C-dimension (in.)[4]	none	EPM-2525	EPM-2525	→	none	EPM-2526	EPM-2525	none	→
Coat	42% KOH	→	→	→	→	→	→	→	→
Electrolyte									

Notes:

- [1] including additives
- [2] full/half-end electrode thickness
- [3] K = mass ratio of active zinc to active silver
- [4] C = internal thickness of the cell case
- [5] V1A is the same as V1, except without mercury.
- [6] five electrodes (3 full in the center of the pack and 2 halves at each end)
- [7] Refer to Table 2, note [5].
- [8] 5-mil nonwoven nylon (Pellon) bag
- [9] → means repeat the value to the left.

The cell manufacturing part of this task was completed on 15 November 1991. The order of operations was as shown below.

1. Coating of cellophane and Celgard with EPMS
2. Cutting of all separators to size
3. Manufacture of positive electrodes
4. Manufacture of mold-pressed negatives
 - a. with solvent-based EPM (No. 2029)
 - b. with water-based EPM (No. 2010)
5. Manufacture of pasted negatives
 - a. with HgO
 - b. with no additive
 - c. with Bi₂O₃
6. Coating of negative electrodes
7. Electrode wrapping
8. Final cell assembly

Except for the added coating operations (numbers 1 and 6 above), that order is the same as for the manufacture of standard cells.

TASK 7: CELL TESTING

Cell testing was started on 18 November 1991 and continued as outlined in Appendix A of this report. The cell numbers corresponding to each variation, as well as their expected initial capacity, are listed in Table 4 below.

Due to poor performance, tests on six of the variations (refer to Chapter 4, Cycles 1 and 2) were discontinued. The cells of the remaining three variations (V1, V2, and V7) were divided into two groups (A and B) and tested as scheduled (refer to Appendix A). Although Group A tests lasted until mid-May, three months beyond the period of performance of the SBIR contract, YTP completed them on its own initiative because of the interest created in the performance of the above cells, particularly those of variation V2. All test results are given in Chapter 4 of this report.

TABLE 4. CELLS TESTED

Variation No.	Cell No.	Expected Capacity (Ah)
V1	1, 2, 19, 20	10.3
V1A	3, 4, 21, 22	10.3
V2	5, 6, 23, 24	12.6*
V3	7, 8, 35, 36	12.6
V4	9, 10, 27, 28	10.3
V5	11, 12, 29, 30	11.2
V6	13, 14, 31, 32	12.6
V7	15, 16, 33, 34	11.2
V8	17, 18, 35, 36	10.3

* The expected initial capacity of this variation, which is dependent on the amount of active silver in the cells, was not affected by the error described in Chapter 3, Task 6.

CHAPTER 4

RESULTS ACHIEVED

The results of the cell tests conducted in accordance with the program detailed in Appendix A are described in this chapter. Also included are the observations regarding the dissection of cells.

FIRST FORMATION CYCLE

The results of this cycle are shown in Table 5. Diversities in the output capacity of identical cells, as seen in Table 5, are not uncommon during the first formation cycle and normally are not a cause of concern. However, variation V3 exhibited very low capacities at 4.0 A, and the outputs were only near normal when the rate was reduced to 1.0 A. This is an indication of high internal resistance and is peculiar. After the end of this cycle, the electrolyte levels of all the cells were adjusted to near the tops of the respective plates to ensure that each cell was sufficiently filled.

SECOND FORMATION CYCLE

Test results on this cycle are summarized in Table 6. Note that the cells were not drained at 1.0 A as in the previous cycle. While variations V1, V2, and V7 performed according to expectations, all the others appeared to experience problems.

1. Variation V1A included three cells doing relatively well, but cell No. 4 delivered only 70 percent of the average capacity of others in the group.
2. Variation V3 was obviously afflicted by high internal resistance.
3. Variation V4 yielded an average capacity of only 68 percent of the expected value.
4. Variation V5 did even worse at 60 percent.
5. Variation V6 included a bad cell (No. 13) with nearly zero capacity; however, the other three cells were also doing poorly at 58 percent of the expected output.
6. Finally, variation V8--containing bismuth oxide as an additive to the zinc electrode--was delivering only about 66 percent of the anticipated capacity.

TABLE 5. CYCLE F-1

Vari- ation No.	Cell No.	Output (Ah)		
		At 4.0 A	At 1.0 A	Total
V1	1	10.39	0.23	10.62
	2	9.96	0.18	10.14
	19	7.00	0.27	7.27
	20	9.65	0.14	9.79
	Avg	9.25	0.21	9.46
V1A	3	10.13	0.10	10.23
	4	5.74	1.00	6.74
	21	10.49	0.13	10.62
	22	10.75	0.13	10.88
	Avg	9.28	0.34	9.62
V2	5	11.05	0.22	11.27
	6	10.65	0.24	10.89
	23	12.11	0.14	12.25
	24	11.19	0.16	11.35
	Avg	11.25	0.19	11.44
V3	7	0.12	9.80	9.92
	8	0.22	9.92	10.14
	25	0.07	8.84	8.91
	26	0.15	9.51	9.66
	Avg	0.14	9.52	9.66
V4	9	7.31	0.76	8.07
	10	8.93	0.44	9.37
	27	8.25	0.49	8.74
	28	8.81	0.48	9.29
	Avg	8.83	0.54	8.87
V5	11	9.18	1.02	10.20
	12	7.68	1.46	9.44
	29	8.85	0.94	9.79
	30	9.42	0.79	10.21
	Avg	8.86	1.05	9.91
V6	13	0.50	3.00	3.50
	14	10.43	1.59	12.02
	31	8.18	1.41	9.59
	32	9.16	1.48	10.64
	Avg	7.07	1.87	8.94
V7	15	9.23	0.93	10.16
	16	8.40	2.08	10.48
	33	8.02	0.37	8.39
	34	7.45	0.46	7.91
	Avg	8.28	0.96	9.24
V8	17	6.99	0.12	7.11
	18	6.83	0.09	6.92
	35	5.47	0.64	6.11
	36	6.76	0.10	6.86
	Avg	6.51	0.24	6.75

TABLE 6. CYCLE F-2

Vari- ation No.	Cell No.	Output (Ah) at 4.0 A
V1	1	10.47
	2	10.09
	19	9.79
	20	10.56
	Avg	10.23
V1A	3	9.08
	4	6.89
	21	9.90
	22	10.66
	Avg	9.13
V2	5	12.39
	6	12.21
	23	13.05
	24	12.46
	Avg	12.53
V3	7	0.23
	8	0.16
	25	0.12
	26	0.27
	Avg	0.20
V4	9	6.08
	10	7.63
	27	6.95
	28	7.39
	Avg	7.01
V5	11	6.92
	12	6.23
	29	6.82
	30	7.04
	Avg	6.75
V6	13	0.24
	14	8.05
	31	6.79
	32	6.98
	Avg	5.52
V7	15	10.46
	16	8.88
	33	9.01
	34	8.72
	Avg	9.27
V8	17	7.19
	18	6.92
	35	6.11
	36	6.86
	Avg	6.77

THIRD FORMATION CYCLE

A third formation cycle was run on all the cells as planned (see Appendix A) except that, in view of the above, the charge was done at 0.3 A and at 50 °C in an attempt to improve charge acceptance and to reduce the internal resistance of the cells--in particular those with EPMS. In addition, the cells were drained at 1.0 A. The results are shown in Table 7.

Variations V1, V2, and V7 continued to perform according to expectations.

Among the other variations, V6 exhibited some improvement because of a rebound in the capacity of cell No. 13 (the other cells actually lost capacity), and V8 did noticeably better at 81 percent of the anticipated capacity. Variations V3 and V5 showed no amelioration of performance, while V1A and V4 did worse than in previous cycles.

CYCLES 1 AND 2

These cycles were performed as outlined in Appendix A and the results can be found in Table 8. It is evident that variations V1, V2, and V7 continued to perform normally. All the other variations did poorly, and it was deemed pointless to continue testing them.

GROUP A TESTS

These tests consisted of sets of 14 consecutive shallow cycles at 50 percent depth of discharge* followed by one deep cycle. They were performed on variations V1, V2, and V7 in accordance with the procedures described in Appendix A.

Each cell was tested until it could no longer deliver its respective shallow cycle capacities (voltage below 1.10 V at the end of discharge). This occurred at the cycle numbers listed below:

Cell No.	Variation No.	Failed Cycle No.
16	V7	80
15	V7	82
1	V1	94
2	V1	96
5	V2	159
6	V2	162

Table 9 and Figure 1 show the outputs obtained on the deep discharges compared to the baseline capacity, which is defined as the average capacity for the same cells in cycles 1 and 2.

* Assuming nominal capacities of 7.91, 9.72, and 8.66 Ah for variations V1, V2, and V7, respectively, based on a utilization of 286 mAh per gram of active silver (equivalent to 3.50 g/Ah, typical YTP criterion to determine the nominal capacity of long-life cells)

TABLE 7. CYCLE F-3

Vari- ation No.	Cell No.	Output (Ah)		
		At 4.0 A	At 1.0 A	Total
V1	1	9.31	0.08	9.39
	2	9.86	0.12	9.98
	19	9.06	0.34	9.40
	20	9.45	0.46	9.91
	Avg	9.42	0.25	9.67
V1A	3	8.20	0.08	8.28
	4	5.16	0.08	5.24
	21	7.29	0.37	7.66
	22	8.55	0.22	8.77
	Avg	7.30	0.19	7.49
V2	5	12.25	0.26	12.51
	6	12.41	0.21	12.62
	23	12.96	0.15	13.11
	24	12.58	0.22	12.80
	Avg	12.55	0.21	12.76
V3	7	0.18	3.34	3.52
	8	0.15	2.83	2.98
	25	0.14	2.85	2.99
	26	0.23	2.94	3.17
	Avg	0.18	2.99	3.17
V4	9	2.69	0.16	2.85
	10	3.99	0.08	4.07
	27	4.11	0.04	4.15
	28	4.11	0.03	4.14
	Avg	3.73	0.08	3.80
V5	11	5.84	0.32	6.16
	12	5.67	0.31	5.98
	29	6.13	0.10	6.23
	30	6.75	0.02	6.77
	Avg	6.10	0.19	6.29
V6	13	2.91	1.78	4.69
	14	8.28	0.40	8.68
	31	5.56	0.07	5.63
	32	6.60	---	6.60
	Avg	5.84	0.56	6.40
V7	15	8.96	0.34	9.30
	16	8.96	0.39	9.35
	33	9.17	0.49	9.66
	34	9.50	0.48	9.98
	Avg	9.15	0.42	9.57
V8	17	8.67	0.04	8.71
	18	8.91	0.01	8.92
	35	7.31	0.08	7.39
	36	8.16	0.08	8.24
	Avg	8.26	0.06	8.32

TABLE 8. CYCLES 1 AND 2

Vari- ation No.	Cell No.	Output (Ah)	
		Cycle 1	Cycle 2
V1	1	9.22	9.58
	2	9.84	9.95
	19	9.64	9.84
	20	9.82	9.73
	Avg	9.63	9.78
V1A	3	4.35	3.47
	4	1.87	0.87
	21	4.55	2.87
	22	5.45	4.35
	Avg	4.06	2.89
V2	5	12.25	12.37
	6	12.39	12.57
	23	12.65	12.73
	24	12.58	12.64
	Avg	12.47	12.58
V3	7	0	0
	8	0	0
	25	0	0
	26	0	0
	Avg	0	0
V4	9	2.46	0
	10	2.95	0.40
	27	3.20	0.19
	28	3.04	0.78
	Avg	2.91	0.34
V5	11	4.21	3.20
	12	4.99	4.20
	29	5.75	1.58
	30	6.25	4.71
	Avg	5.30	3.42
V6	13	1.24	0.50
	14	0	0
	31	3.52	0.78
	32	5.54	4.24
	Avg	2.58	1.38
V7	15	9.35	10.21
	16	9.19	9.92
	33	9.11	9.72
	34	8.67	9.74
	Avg	9.08	9.90
V8	17	6.51	6.83
	18	6.04	6.18
	35	4.76	4.92
	36	4.89	5.00
	Avg	5.55	5.73

TABLE 9. CAPACITY IN DEEP CYCLES⁽¹⁾

Variation No. Cell Nos.	V1 1-2	V2 5-6	V7 15-16
Baseline Capacity ⁽²⁾			
Ah	9.71	12.53	9.49
mAh/g ⁽³⁾	351	369	313
<i>Deep Cycle Capacity</i>			
CY 15	Ah	7.75	10.84
	% ⁽⁴⁾	79.8	86.5
	mAh/g ⁽³⁾	280	319
CY 30	Ah	6.65	9.76
	% ⁽⁴⁾	68.5	77.9
	mAh/g ⁽³⁾	240	287
CY 45	Ah	5.96	9.04
	% ⁽⁴⁾	61.4	72.1
	mAh/g ⁽³⁾	215	266
CY 60	Ah	5.12	8.47
	% ⁽⁴⁾	52.7	67.6
	mAh/g ⁽³⁾	189	249
CY 75	Ah	4.71	7.75
	% ⁽⁴⁾	48.5	61.9
	mAh/g ⁽³⁾	170	228
CY 90	Ah	4.29	7.28
	% ⁽⁴⁾	44.2	58.1
	mAh/g ⁽³⁾	155	214
CY 105	Ah		6.73
	% ⁽⁴⁾		53.7
	mAh/g ⁽³⁾		198
CY 120	Ah		6.29
	% ⁽⁴⁾		50.2
	mAh/g ⁽³⁾		185
CY 135	Ah		5.78
	% ⁽⁴⁾		46.1
	mAh/g ⁽³⁾		170
CY 150	Ah		5.34
	% ⁽⁴⁾		42.6
	mAh/g ⁽³⁾		157

Notes:

- [1] All data points represent the average of two cells.
- [2] Average capacity of cycles 1 and 2 (see Table 3)
- [3] Milliamperes-hours per gram of active silver
- [4] Percent of baseline capacity

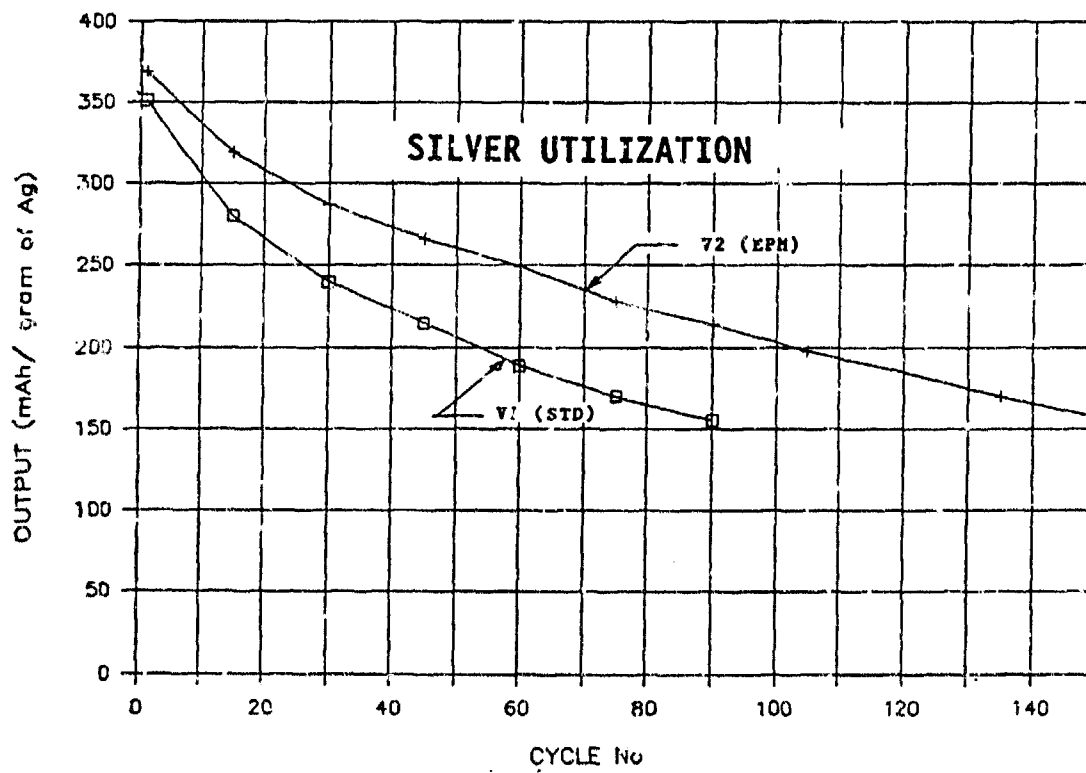
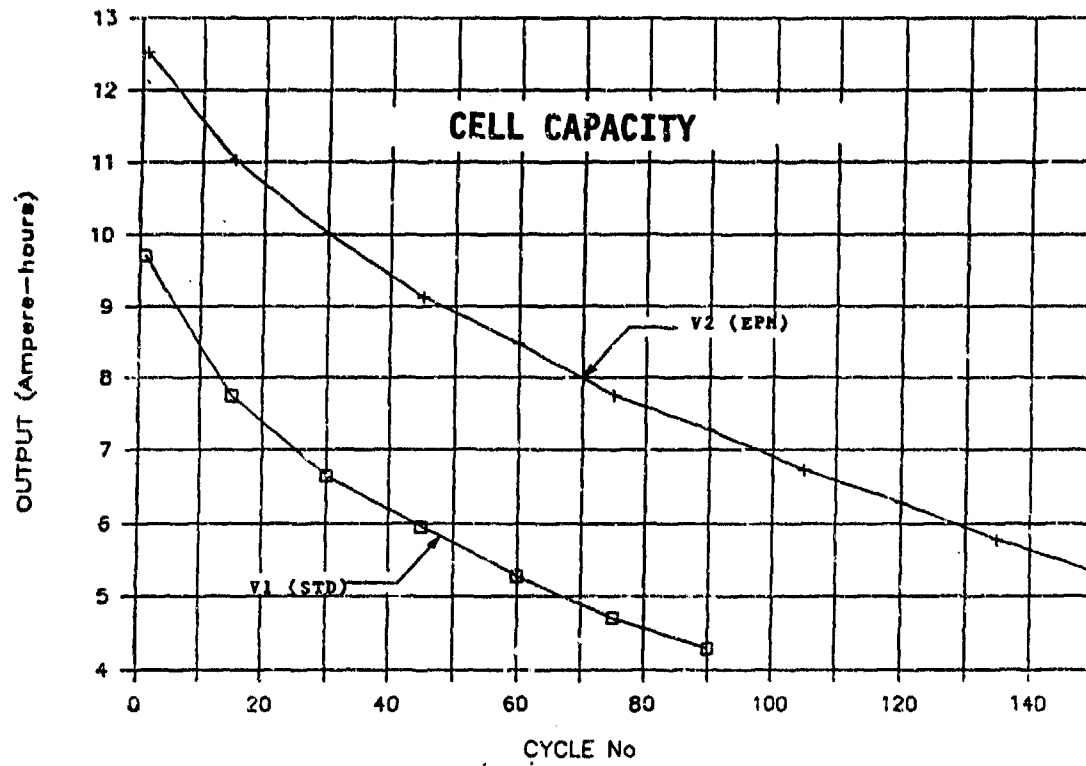


FIGURE 1. CAPACITY IN DEEP DISCHARGES (FOUR-AMPERE RATE)

GROUP B TESTS

Group B cells completed the characterization cycles detailed in the test program (see Appendix A). The results are summarized in Tables 10 through 18 below and are expressed as average values of the two cells of each variation. YTP followed this procedure rather than reporting individual cell data because, throughout the entire program, the differences between those two cells were quite small.

TABLE 10. CYCLE 3 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Gas evolution [1]			
cm ³ /hr, maximum	0.50	0.19	0.31
cm ³ /hr, average	0.43	0.16	0.20
cm ³ /hr x g Zn, average	18.3 x 10 ⁻³	5.5 x 10 ⁻³	7.7 x 10 ⁻³
Discharge (4.0 A at 25 °C)			
V peak[2]	1.499	1.496	1.495
V minimum	1.475	1.472	1.475
Ah	9.70	12.41	9.70
mAh/g silver	350	365	320

Notes:

[1] last 8 hours of a 24-hour stand at 38 °C

[2] peak of silver monoxide plateau

TABLE 11. CYCLE 4 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at 25 °C)			
V peak	1.500	1.496	1.496
Ah	9.65	12.39	9.72
mAh/g silver	348	364	321
Gas evolution [1]			
cm ³	2.2	0.8	1.1
cm ³ /g zinc	0.094	0.028	0.042

Notes:

[1] total for the entire discharge

TABLE 12. CYCLE 5 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at 0 °C)			
V minimum	1.424	1.417	1.412
Ah ^[1]	8.64	10.85	8.60
mAh/g silver ^[1]	312	319	284

Notes:

[1] drain at 4.0 A, 25 °C not included

TABLE 13. CYCLE 6 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at 25 °C)			
Ah	9.27	12.05	9.36
mAh/g silver	335	354	309

TABLE 14. CYCLE 7 DATA SUMMARY (GROUP B TESTS)
[SEE ALSO FIGURE 2]

Variation Number	V1	V2	V7
Discharge (8.0 A at 25 °C)			
V minimum	1.436	1.435	1.429
Ah ^[1]	8.80	11.57	8.99
mAh/g silver ^[1]	318	340	297

Notes:

[1] drain at 4.0 A, 25 °C not included

Cycle 7

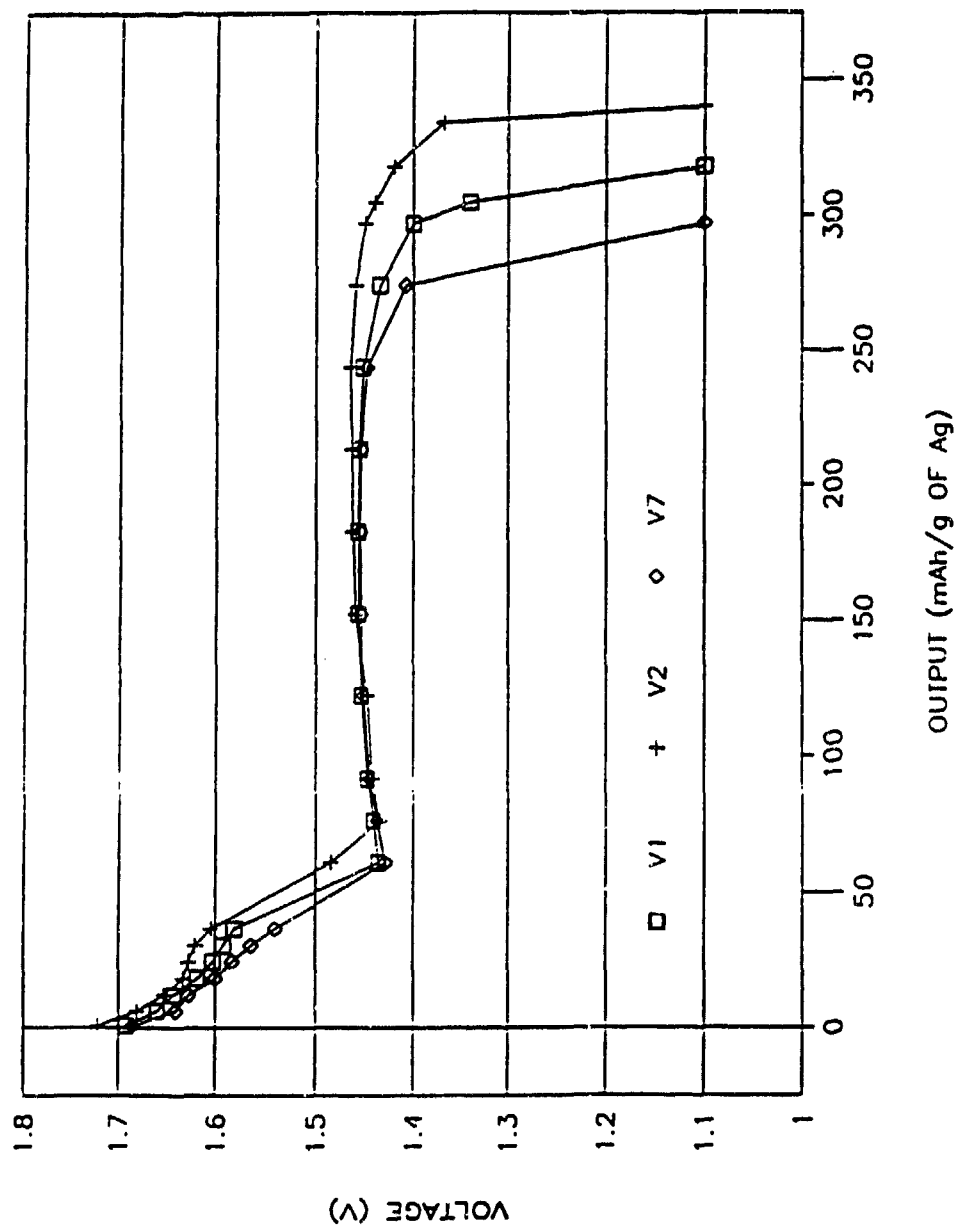


FIGURE 2. DISCHARGE AT EIGHT AMPERES

TABLE 15. CYCLE 8 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (12.0 A at 25 °C)			
V minimum	1.407	1.411	1.403
Ah ^[1]	8.35	11.05	8.45
mAh/g silver ^[1]	301	325	279

Note:

[1] drain at 4.0 A, 25 °C not included

TABLE 16. CYCLE 9 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at 25 °C)			
V minimum	1.471	1.473	1.470
Ah	8.64	11.63	8.79
mAh/g silver	312	342	290

TABLE 17. CYCLE 10 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at -20 °C)			
V minimum	1.209	1.128	1.175
Ah ^[1]	7.36	8.55	6.81
mAh/g silver ^[1]	266	251	225

Note:

[1] drain at 4.0 A, 25 °C not included

TABLE 18. CYCLE 11 DATA SUMMARY (GROUP B TESTS)

Variation Number	V1	V2	V7
Discharge (4.0 A at 25 °C)			
Ah	8.02	11.27	8.20
mAh/g silver	290	331	271

CELL DISSECTION

Cell Numbers 3(V1A), 7(V3), 9(V4), 11(V5), 13(V6), and 17(V8) were dissected to investigate the causes of their poor performances. The following was noted:

- None of the cells appeared to have developed internal shorts as all obvious signs of such (perforation of the separators, adhesion of separators to the electrodes, presence of nodes of zinc at the positive electrodes, penetration of silver through all separator layers) were absent.
- All separators were mechanically strong, flexible, and wet with electrolyte.
- No obvious manufacturing defects were found.
- The negatives of cell No. 3 appeared fully discharged, while the positives retained a high percentage (≈ 80 percent) of their charge, as indicated by their black/grey color, and by dummy discharge* results.
- In all the cells containing EPM-coated negatives (Nos. 7, 9, 11, and 13), the coating had formed a thick black layer that could easily be separated from the electrode.
- Cell No. 17, with Bi_2O_3 in the negative, appeared to be normal except that (1) the fifth (outermost) layer of C-19 (facing the negatives) was black and (2) there were also black spots in the fourth layer.

Cell pairs 1, 2(V1); 5, 6(V2); and 15, 16(V7) were dissected after removal from the automated test station at the completion of Group A cycling.

The failure of the V1 and V7 cells was obviously due to "shape change" of the negative electrodes. This was evident as about 50-60 percent of the collector was devoid of active material at the top and edges of the plate while the center was heavily densified. The positive electrodes facing the bare areas of the collector remained charged--as evidenced by their black color, indicative of the presence of silver oxides--even though the cells were disassembled in the discharged condition.

The reasons for the failure of the V2 cells were less obvious. The "shape change" of the negative electrodes was limited to 20 percent at the most, clearly not enough to cause failure. Although there were no apparent shorts in either cell and the EPM-coated Celgard 2500 was mechanically strong, it was loaded with silver and the concentration may have been enough to create a diffuse, high-resistance, internal short. However, based on the shape of the capacity vs. cycle life curve (Figure 1),** it is far more likely that the failure was due to a slow passivation of the negative electrode active material.

* Forced discharge against inert counter-electrodes

** The curve for the subject cells has a normal downward slope. A short, even if very slow, would create a deflection in the curve, corresponding to an accelerated rate of decline.

CHAPTER 5

EVALUATION OF THE RESULTS

The evaluation of the test data presented above led to the finding that the performance of the cells with EPMs, with the exception of V2, was disappointing to the point that testing on those variations (V3, V4, V5, and V6) had to be terminated. This prompted an investigation of the reasons for the anomaly; the results of that study provide an explanation of what happened.

As previously stated in Chapter 3, Task 6, variation V2 cells were fabricated with negative plates left over from a previous EPM test because of a mix-up by manufacturing personnel. These plates, which physically are very similar to the V2P plates (same dimensions, 5 percent heavier), contain 3.8 percent of a solvent-based EPM designated as No. 17K and have no EPM coating. All other cell components were in accordance with the Cell Design Details (Table 3).

No. 17K was one of the early generation EPMs developed by Mr. Robert Peck that was tested by YTP on a limited scale during the time between the submission of its Phase I SBIR proposal and the award of the contract. Although the preliminary results of these tests were promising, the formulation was not proposed for study under this program because the other formulations were considered to be more advanced, with longer cycle life expectancies than No. 17K.

The final results of those in-house tests, which were limited to life cycling three cells with a separator system consisting of two turns of EPM-coated Celgard 2400, paralleled those obtained on the V2 cell except that the failure mode was internal shorting that occurred at cycles 78, 79, and 120, respectively.

A study of the voltage characteristics of the other variations with EPMs indicates that each one had high internal resistance from the start (variation V3) or developed it after just a few cycles. This characteristic is almost certainly an unwanted effect of the presence of the EPMs; it manifests itself as an unusually low-load voltage at the beginning of discharge (e.g., 1.15 V as compared to a normal voltage of 1.48-1.50 V* at 4.0 A), followed by a brief partial recovery and by a further decline that leads to an early cutoff.

Dissection results indicate that the problem was caused by the EPM used to coat the negatives (No. 2029), which seemed to condense into a thick insulating layer (see Chapter 4, "Cell Dissection"). Further evidence in that direction is that those cells

* Fresh silver-zinc cells normally show a silver-peroxide voltage at the beginning of discharge that is even higher, usually 1.70 - 1.80 V at 4.0 A (see Figure 2).

that also contained EPM No. 2029 as an additive to the negative electrode (variation V3) had the worst performance of all the cells tested.

YTP consulted with the inventor, Mr. Robert Peck, who concluded, based on the analysis of leftover EPMS, that an error in formulation resulted in solvent being trapped within the pores of the active material and creating high-resistance gaps between it and the EPMS. This constituted a barrier for the flow of OH⁻ ions that is necessary for normal cell operation.

To avoid the repetition of events such as those described above, YTP intends to devise and implement appropriate screening tests for the EPMS and, as deemed necessary, for the electrodes and separators containing them. A section of YTP's Phase II SBIR proposal outlines the planned quality control effort.

The EPMS used to coat the separators (Nos. 2525 and 2526), made to different formulations, did not suffer from the same problem as far as YTP can determine. This is obvious in the case of No. 2525, used in V2 cells, which performed successfully.

CHAPTER 6

CONCLUSIONS

The conclusions drawn from Phase I of this SBIR program are detailed in the following subparagraphs. As stated in Chapter 3, Task 7, and foreseen in YTP's proposal, the test program on Group A cells extended for approximately three months beyond the period of performance of this contract and was completed on the company's own initiative.

EPMs

Electrical Performance

Electrical tests performed on the only viable variation of cells with EPMs (V2) were quite encouraging and justify the expectations stated in YTP's SBIR proposal as well as those originated by preliminary tests performed in the six-month period prior to the award of the Phase I contract. In Group A testing, V2 cells run well ahead of the standard cells in the following areas, as shown in Table 9 and Figure 1.

- They had a 68 percent longer cycle life (160 vs. 95).
- They had a 32 percent better silver utilization after 60 cycles and a 38 percent better utilization after 90 cycles.
- The overall capacity was 62 percent better after 60 cycles and 70 percent better after 90 cycles. This margin is very important because it reflects the actual capacity improvement realized in cells of the same external configuration. The improvement results from the combination of a better silver utilization and the additional amount of active materials made possible by using thinner separators.
- The 160 cycles obtained were far more than ever achieved from silver-zinc cells with main separators of the same thickness (less than 0.1 mm).

The performance in Group B testing of cells with EPMs also compares favorably to that of the standard (V1) cells.

- Gas evolution on charged stand and on discharge was only about 30 percent that of the standard cells. This is a very welcome result that is taken as evidence of the lower solubility of negative active material in the electrolyte, which translates into a reduced rate of shape change and, therefore, longer cycle life.

- Voltages at 4.0, 8.0, and 12.0 A were essentially the same as for the standard cells, indicative of good high-rate discharge performance.
- Low temperature performance was good at 0 °C but only fair at -20 °C, where the minimum voltage was 80 millivolts below the standard cell voltage. This is an admitted shortcoming of the EPMS that requires corrective work.

On the negative side, four out of five cell variations containing EPMS never made it past the formation cycles, and the same would likely have happened to the fifth variation (V2) but for a fortunate error committed by manufacturing personnel. A detailed discussion of this problem appears in the "Formulations" subsection below.

Manufacturing

The manufacture of negative electrodes containing or coated with EPMS, as well as the coating of separators, is simple enough in small quantities (see Chapter 3, Task 2), and the procedures used can easily be extended to pilot plant quantities. If only the coating of plates and/or separators will be required, the scaleup to production quantities should not involve any significant technical problems.

However, the scaleup of composite plates to full production may be more difficult, especially for solvent-based EPMS, which would require an elaborate ventilation system to remove the solvent* from the work areas. Unfortunately, the V2 formulation falls into this category. For this reason, YTP's Phase II proposal leans heavily on water-based EPMS.

While EPMS can be readily compounded with dry zinc or zinc-oxide powders, it may be more awkward to do so in a wet paste (as used for mass production) because of the possible difficulties in obtaining a truly homogeneous mixture.

Scaleup to production quantities should be further investigated as part of a Phase II program.

Formulations

As the EPMS are still at a relatively early state of development, the formulations are periodically being improved and diversified as the number of potential applications increases. Although this situation is desirable in the long term, it may create occasional short-term problems such as experienced during this program; errors in formulation, mixing procedure, or curing temperature can change the properties of the materials, which may then lose their effectiveness or even become harmful as they have the potential of acting as electrical insulators.

As the development of the EPMS continues, it will be necessary to evolve and implement quality control procedures to ensure that the EPMS consistently function as intended (see Chapter 5, seventh paragraph).

* The solvent used, N-methyl-2-pyrrolidone, presents no known health hazards, except in high concentrations.

BISMUTH OXIDE (Bi_2O_3)**Electrical Performance**

The initial performance of the cells with Bi_2O_3 (variation V8) was quite poor in terms of capacity delivered, which was only 71.4 percent of that of the standard cells during cycle F-1. Although they improved to 86.0 percent during cycle F-3 (charge run at 50 °C), they settled back to an average of 58.1 percent during cycles 1 and 2. As a result, the tests were discontinued.

It should be noted that these cells did not exhibit a high internal resistance problem; their discharge voltage was normal.

The observations made during dissection did not uncover any obvious abnormality. The black color seen in the fifth layer and part of the fourth layer of C-19 (see Chapter 4, "Cell Dissection") is probably due to a chemical reaction between bismuth and the polymeric chain of the cellophane and is not necessarily harmful to cell performance. (Cellophane is known to react with several metals, including silver and titanium. The compounds so formed actually increase its resistance against oxidation).

Looking again at the performance data, it appears that the formulation used for the negative electrodes (10 percent Bi_2O_3 and no mercury) reduces their charge acceptance. It is worth noting that

- Essentially all of the input capacity was available for discharge, and
- The input capacity was best at lower rates (0.3 A vs. 0.5 A) and at higher temperatures (50 °C vs. 25 °C).

It is possible that formulations containing less Bi_2O_3 (2-5 percent) will perform better on fresh cells. If so, they should be tested for the claimed benefit of the additive (a slower rate-of-shape change for the zinc electrode).

Manufacturing

As explained in Chapter 3, Task 2, Step 3, the manufacture of electrodes with 10 percent (or less) Bi_2O_3 does not present any problem. Existing mass production methods are readily adaptable to the introduction of Bi_2O_3 into the zinc oxide mix for pasting.

RAI P2291-40/20 SEPARATOR

The electrical tests on cells with a combination of three turns of this separator, described in Chapter 2, "Improvements to the Separators," and two turns of C-19 (variation V7) have been completed. The combination offers the advantage of allowing for almost 10 percent extra active materials because it takes up less space than the standard separator. However, the V7 cells started with 11 percent lower silver utilization than the standard cells (see Table 9). As a result, their initial capacity was slightly lower. After 60 cycles, they were 4.7 percent higher in capacity, but their silver utilization remained lower--albeit by a reduced margin of only

6.3 percent. Their cycle life was actually shorter than that of the standard cells by 15 percent on the average (81 vs. 95 cycles).

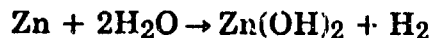
An analysis of cell performance in Group B testing, compared to that of the standard cell, leads to the following:

- The gas evolution during charged stand and discharge was much lower, only about 40-45 percent. Based on those results alone, YTP would have expected a difference in the rate of capacity loss in favor of the V7 cells, but this did not materialize.
- The high rate and low temperature voltages were consistently lower, but the difference was so small that it is hardly significant. The only exception was the -20 °C discharge where the voltage was 34 millivolts lower. The capacity was also more severely affected at that temperature.

CELLS WITHOUT MERCURY

The cells of this variation (V1A) were identical in construction to the standard cells (V1) in every respect except for the absence of mercury (or any substitute thereof) in the negative electrodes. Although this was not mentioned in YTP's SBIR proposal, YTP decided to build them as a baseline for other cell variations lacking mercury in the negatives, i.e., V4, V5, V6, and V8. (V2 and V3 had no mercury either, but the EPMs included in their formulation were expected to constitute a more than adequate replacement.)

The mercury in zinc/zinc-oxide electrodes acts as an anticorrosive agent by amalgamating with the zinc and preventing or slowing the self-discharge reaction:



Not unexpectedly, the cells of this variation lost capacity faster than the standards; however, the rate of loss was much faster than anticipated, probably accelerated by the cycle F-3 charge done at 50°C. The capacity data of Tables 4 to 7, summarized below, shows how quick the loss was:

Cycle No.:	F-1	F-2	F-3	1	2
% of standard cell output:	101.7	89.2	77.5	55.0	35.0

Testing was discontinued after Cycle 2, and Cell No. 3 was dissected (see Chapter 4, "Cell Dissection"). Not surprisingly, the effects of the zinc corrosion were plainly in view as soon as the cell was opened- the positives retained about 80 percent of their charge, while the negatives appeared fully discharged.

CHAPTER 7

RECOMMENDED ACTIONS

Based on the conclusions reached, detailed in the preceding chapter, the following action items are recommended. Note that the first one is already being implemented at YTP's own initiative, while the remaining items are included in the company's Phase II proposal.

BUILD ADDITIONAL CELLS

As part of YTP's ongoing internal research and development program, a new group of 28 cells is presently being tested. This group is divided into seven variations of four cells each. Included in this group are three variations with EPMS (one new and two that are based on formulations successfully tested in the past), one variation with 5 percent Bi_2O_3 and 1 percent HgO in the negatives, and three variations not involving EPMS.

FURTHER DEVELOPMENT WORK

This work is intended as part of a Phase II SBIR program and is fully described in YTP's proposal for that program (June 1992). The main objectives of the Phase II work are the following:

1. To demonstrate that improvements beyond those achieved in Phase I are possible
2. To extend those improvements to large cells (see next item, "Extension of Manufacturing Techniques")
3. To develop manufacturing procedures adaptable for the production of large quantities of cells
4. To develop the necessary quality control procedures to ensure the reliability of the cells and the reproducibility of the test results

During the initial stages of this program, through the manufacture of a group of small (8.5 ampere-hour nominal) cells, YTP plans to determine the benefits derived from EPMS used in the following three different capacities:

- As an additive to the negative electrodes
- As a coating for the negative electrodes
- As a coating for the separators

After those cells are tested and the results are analyzed, YTP is proposing to combine the better-performing variations in a second group of 8.5 ampere-hour cells using EPMS in two or all three capacities to establish whether or not the benefits are additive or synergistic. The same strategy is applicable to negative electrode additives other than EPMS.

To conclude the Phase II program, YTP is projecting to build a group of 190 ampere-hour cells (presently used for torpedo target propulsion) to uncover and resolve any scaleup problems and to serve as demonstration models and as a baseline for any further efforts, possibly including a Phase III program.

EXTENSION OF MANUFACTURING TECHNIQUES TO MASS PRODUCTION

The completion of the efforts described above must lead to a decision on which of the improvements achieved should be implemented in YTP's standard line of silver-zinc batteries and which should be limited to special cells only. As with all business decisions, this one will require a thorough cost-benefit analysis.

Included in that decision must be a clear understanding of the total costs involved in (1) the conversion of existing manufacturing facilities to the new processes or (2) the construction of new facilities.

As stated elsewhere in this report, some of the improvements may be achieved with little or no change to existing facilities, while others may require extensive change or complete rebuilding.

APPENDIX A

TEST PROGRAM

All cells will be submitted to two formation cycles and two test cycles (see Table A-1).

TABLE A-1. FORMATION AND TEST CYCLES (ALL CELLS)

Cycle No.	Charge		Discharge		Drain ^[3]	
	Current (A)	FOCV	Current (A)	EODV	Current (A)	EODV
F-1	0.3	2.10	4.0	1.10	1.0	1.10
F-2 ^{[1],[2]}	0.4	2.05	4.0	1.10	---	---
1-2	0.5	2.05	4.0	1.10	---	---

Notes:

- (1) If any cell performs below expectations during this cycle, all cells will be given a third formation cycle that is the same as F-2.
- (2) Electrolyte amounts will be adjusted at the end of the charge to a level near the tops of the plates. Earlier adjustments may also be required after the soaking period and at the end of the first formation charge. However, no adjustments will be made after formation, except for compelling reasons.
- (3) When the 4-A discharge has reduced cell voltage to 1.10, the current is lowered to 1 A and the discharge ("drain") is continued, again to a 1.10-V cutoff.

At the end of Cycle 2, the cells will be divided into two groups of 18 cells (two cells of each variation per group) and tested as described in the following two subsections.

GROUP A

Group A is to be cycled using a computer-controlled, automatic cycler at the following regime:

Cycles 3-14: Charge at 0.50 A to 2.05 V
Rest two hours
Discharge at 4.0 A for 59, 65, or 73 minutes*
Rest four hours

Cycle 15: Same as above, except continue discharge to 1.10 V

Cycles 16-29, 31-44,
46-59, etc.: Repeat cycles 3-14

Cycles 30, 45, 60,
75, etc.: Repeat cycle 15

The regime will be continued until all the cells fail to deliver their shallow cycle capacity. As the cells fail, they will be removed from the test and dissected to determine the cause of failure.

GROUP B

Group B is to be used for characterization purposes (including gas evolution, low temperature, and high-rate discharge). The tests listed in the notes for Table A-2 are to be performed (all charges and discharges to be terminated at 2.05 V and 1.10 V, respectively). All charges are to be done at 25 °C.

Cycle 3 (gas evolution measurement) consists of the following:

- Charge at 0.50 A,
- Stabilize at 38 °C (100 °F) for 24 hours and measure gas evolution with a eudiometer during the last 8 hours,
- Cool to room temperature and discharge at 4.0 A.

* Variations V1, V1A, V4, and V8: 59 minutes
Variations V2, V3, and V6: 73 minutes
Variations V5 and V7: 65 minutes

TABLE A-2. GROUP B TESTING

Cycle No.	I_c (A)	I_d (A)	Discharge Temperature (°C)	Notes
4	0.50	4.0	25	[1]
5	0.50	4.0	0	[2], [3]
6	0.50	4.0	25	-----
7	0.50	8.0	25	[3]
8	0.50	12.0	25	[3]
9	0.50	4.0	25	-----
10	0.50	4.0	-20	[2], [3]
11	0.50	4.0	25	-----

Notes:

- [1] Measure gas evolution during the discharge using a eudiometer.
- [2] After charging, insulate the cell with polyurethane foam, place it in a cold box overnight (at least 16 hours), and then discharge it at tabulated temperature.
- [3] After the main discharge is ended, allow the cell to stand at 25 °C for at least eight hours, then determine the residual capacity with a second, 25-°C, 4-A discharge ("drain").

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